United States Patent

Tanabe et al.

[54] THERMOSETTING POLYESTER RESIN
AND POWDER COATING RESINOUS
COMPOSITION CONTAINING THE SAME

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[21] Appl. No.: 560,226

[22] Filed: Jul. 20, 1990

Related U.S. Application Data
[63] Continuation-in-part of Ser. No. 262,734, Oct. 12, 1988,
abandoned.

[30] Foreign Application Priority Data
Feb. 29, 1988 [JP] Japan 63-48412

[51] Int. Cl. 3 C08G 63/00
[52] U.S. Cl. 528/308; 528/272;
528/296; 528/298; 528/299; 528/302;
528/308.1; 528/308.6; 525/418; 525/450;
525/534

[58] Field of Search 528/272, 296, 298, 299,
528/302, 308, 308.1, 308.6, 525/418, 450, 534

References Cited
U.S. PATENT DOCUMENTS
4,352,924 10/1982 Wooten et al.
4,356,285 10/1982 Kumagai
4,397,979 8/1983 Reimschuessel

OTHER PUBLICATIONS

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ABSTRACT
The invention concerns a thermosetting polyester resin capable of forming an anisotropic molten phase comprising a repeating unit of the formula: A-X-B alone, or a combination of the repeating unit of the formula: A-X-B and the repeating unit of the formula: R, adjoining two repeating units being connected each other through an ester bond, in which A represents a mesogenic group defined in the specification, B is a spacer group defined in the specification, X is an ester bond, and R represents a bivalent to hexavalent aliphatic, aromatic or alicyclic hydrocarbon residue, the end bondings of the connected repeating units being occupied by OH, COOH or their reactive derivatives and the sum of the resinous acid value and the OH value being 10 to 200.

The invention also provides a powder coating resinous composition containing the abovesaid resin.

2 Claims, No Drawings
THERMOSETTING POLYESTER RESIN AND
POWDER COATING RESINOUS COMPOSITION
CONTAINING THE SAME

This application is a continuation-in-part of now
abandoned U.S. patent application Ser. No. 07/262,734
filed on Oct. 12, 1988 abandoned.

FIELD OF THE INVENTION

The present invention relates to a novel class of ther-
mosetting polyester resin capable of forming an aniso-
tropic molten phase and having hydroxyl and/or car-
boxyl functional groups and to a powder coating resin-
ous composition containing the same.

BACKGROUND OF THE INVENTION

During these 20 years, various low molecular liquid
crystalline materials have been synthesized and used as
optical display elements for watches, computers, tele-
visions and the like. Regarding to high molecular liquid
crystalline materials, attention has been directed to
studies on thermotropic liquid crystalline materials and
especially on such resins as having improved strength
and thermal resistance under normal conditions and
being easily transformed to molten phase due to liquid
crystal properties thereof, as in all aromatic polyester
resins disclosed in Japanese Patent Application Kokai Nos. 54-50594 and 55-144024. Other high polymers
having thermotropic liquid crystal properties have been
et al, Polymer 24, 1299, 1983 and Kobunshi Kako 34,
[1], 39, 1985 by W. R. Kringsbaum and J. Watanabe. In
these high polymers, liquid crystal properties (Optical
anisotropic properties) are generated, as in low molecu-
lar liquid crystalline materials, by the repeating unit
structure in the main chain comprising a stiff mesogenic
group and a soft spacer group. Since the abovementi-
don main chain type, high molecular liquid crystal-
line materials have, in general, a large orientation time
of molecular motion, they are not always suitable for a
high response display application in contrast to low
molecular liquid crystalline materials. However, re-
search activities have been continued to apply them to
thermal recording medium, wave-selective transmission
or reflecting film and the like to make the most of their
film-forming and filmment forming properties.

However, the proposed liquid crystal polyes-
ters are all of thermoplastic nature. Their end groups
are, in general, blocked ester bonds as acetyl, phenyle-
ster and the like. This is because if there exist end func-
tional groups, the polymers are liable to be pyrolyzed at
the melting points as high as 250° C. Aver-
age molecular weights are also very high, e.g. tens of
thousands to several hundred thousands, so as to be
suitable for fluxing. Thus, the proposed polymers do
not contain any or any substantial quantities of end
functional groups (if any, it is only in the level enough
to give a resins acid value of less than 10), and there-
therefore they can not be used as a thermosetting resin for
coating composition.

Under the circumstances, such polyester resin as
being useful as a thermosetting resin and capable of
forming an anisotropic molten phase at a lower melting
point has been longed for, in paint industries.

In a coating composition area, a thermosetting poly-
ester resin has become the object of public attention as
the main constituting component of powder coating resinous composition.

Coating powders are usually prepared by mixing
resinous component, pigment and other additives,
kneading the mixture at an elevated temperature, cool-
ing the mixture to a solid mass and pulverizing the same.
Therefore, if the employed resinous component is of
thermosetting nature, it must be stable at the melt-
kneading stage, but fully cured by heating at the curing
stage.

In considering powder coating resinous composition
comprising a polyester resin and a melamine resin or
blocked polyisocyanate compound, most of the poly-
esters resins proposed for solvent type coating composi-
tions' are possessed of lower softening points and there-
therefore, when powder coating is prepared with said resins,
blocking of the powder is liable to occur during storage of
said powder. When a polyester resin with a higher
softening point is selected, such resin is easily gelated at
the melt-kneading stage, and therefore, great difficulties
are encountered in the preparation of coating powder.
Even succeeded in obtaining the powder, there are
problems of poor leveling and gloss of the formed coat-
ing.

In U.S. Pat. No. 4,352,924 and EP 0,070,118, are
disclosed thermosetting powder coating compositions
with crystalline polyesters prepared from isophthalic
acid, terephthalic acid and 1,4-cyclohexane dicarboxylic
acid as dicarboxylic acid components and 1,4-
butane diol and 1,6-hexanediol as diol components.
However, it is not yet up to the mark in the sense of
striving for compatibility of blocking resistance of the
powder and leveling of the formed coating.

Furthermore, powder coating comprising a carboxyl
containing polyester resin and a polyepoxy compound
has also been known in the art, as, for example, Japanese
Publication No. 58-29342. Such powder coating is ex-
cellent in mechanical strength, adhesion and anticor-
rosion properties and therefore has been widely used in
various technical fields. Finally, JP 57-198725 discloses
polyesters derived from 4,4-diphenyl dicarboxylic acid
and alkylene glycol, but such polyesters are incapable of
giving an anisotropic molten phase and, further, these
polyesters have a transition point of 250° C. or more.

However, the disclosed powder coatings are all based
on polyester resins with considerably higher acid values,
e.g. 40-70, and therefore, there are problems of inferior
storage stability of the powder and poor leveling
of the formed coating.

It is, therefore, an object of the invention to provide
a novel thermosetting polyester resin which can be used
as a thermosetting resin in the field of coating composi-
tion and especially coating powder and can be trans-
formed to an anisotropic molten phase at a considerably
lower melting temperature. It is an additional object
of the invention to provide a thermosetting resinous com-
position comprising the abovementioned polyester resin
and a hardener, which can be used as the base material
for coating powder. A further object is to provide coat-
ing powder which is free from undesired blocking dur-
ing storage of the powder, easily prepared by a conven-
tional method of melt kneading and capable of resulting
in a coating with excellent leveling and gloss properties.

SUMMARY OF THE INVENTION

According to the invention, the abovementioned
objects are attained by the provision of a thermosetting
polyester resin comprising a repeating unit of the formula: A-X-B, wherein 100 to 50 mol % of A stands for a mesogenic group selected from a polyphenylene group in which 2 or more benzene rings are aligned and connected each other in their respective para-position, a polyphenylene group in which 2 or more benzene rings are aligned and connected each other in their respective para-position through azo, azoxy, azomethine, ester of trans-vinylene bond, or 2,6-naphthylene group, the remaining 50 mol % of A stands for a member selected from the group consisting of p-phenylene, m-phenylene, o-phenylene and trans 1,4-cyclohexylene; B is a spacer group represented by the formula: \(-\text{CH}_2\text{H}_n\), or

\[-\text{CH}_2\text{CH}_2\text{O}_m\text{CH}_2\text{CH}_2\text{H},\]

in which \(n\) is an integer of 2 to 20 and \(m\) is an integer of 1 to 19; and X is an ester bond, adjoining two repeating units being connected through an ester bond, end bondings of the connected repeating units being occupied by OH, COOH or their reactive derivatives, sum of resinous acid value and OH value being 10~200, and being capable of forming an anisotropic molten phase, or a thermosetting polyester resin comprising a combination of a repeating unit of the formula:

\[A-X-B\]

wherein 100 to 50 mol % of A stands for a mesogenic group selected from a polyphenylene group in which 2 or more benzene rings are aligned and connected each other in their respective para-position, a polyphenylene group in which 2 or more benzene rings are aligned and connected each other in their respective para-positions through an azo, azoxy, ester or trans-vinylene bond, or a 2,6-naphthylene group, the remaining 50 mol % of A stands for a member selected from the group consisting of p-phenylene, m-phenylene, o-phenylene and trans 1,4-cyclohexylene; B is a spacer group represented by the formula: \(-\text{CH}_2\text{H}_n\), or

\[-\text{CH}_2\text{CH}_2\text{O}_m\text{CH}_2\text{CH}_2\text{H},\]

in which \(n\) is an integer of 2 to 20 and \(m\) is an integer of 1 to 19; and X is an ester bond, and a repeating unit of the formula: \(R \ldots [II]\), wherein \(R\) stands for bivalent to hexavalent aliphatic, aromatic or alicyclic hydrocarbon residue which may include up to 4 OH and/or COOH group, the weight ratio of said units (I) to units (II) being 9.9:0.1~70:30, adjoining two repeating units placed in random order being connected through an ester bond, and bondings of the connected repeating units being occupied by OH, COOH or their reactive derivatives, sum of resinous acid value and OH value being 30~150, and being capable of forming an anisotropic molten phase.

In this invention, are also provided a powder coating resinous composition comprising either type of the abovementioned polyester resins wherein the end bondings are HO or its reactive derivative and the resinous OH value is 20~200, and blocked isocyanate compound or aminoplast resin, and a powder coating resinous composition comprising either type of the abovementioned polyester resins wherein the end bondings are carboxyl, hydroxyl or methyl ester groups and the

resinous acid value in 15~100, and a polyepoxy compound or resin having 2 or more epoxy groups in the molecule.

The first type of the present polyester resin comprises a repeating unit of the formula: A-X-B, adjoining two repeating units being connected through an ester bond, end bondings of the connected repeating units being occupied by OH, COOH or their reactive derivatives, the sum of resinous acid value and OH value being 10~200 and being capable of forming an anisotropic molten phase.

Such resin has a main chain type, high molecular liquid crystalline structure in which mesogenic groups (A) and spacer groups (B) are alternately arranged and connected with each other through an ester bond, and cross-linkable functional groups such as OH or COOH are contained in a higher concentration in the resin as ester bondings. In that sense, the present resin is clearly distinguished from the heretofore proposed main chain type, high molecular liquid crystalline materials.

Speaking of the constituting component (A) of the present polyester resin, 100 to 50 mol % of said (A) must be a mesogen group selected from the group consisting of a polyphenylene group in which 2 or more benzene rings are aligned and connected each other in their respective para-position, as, for example, 4,4'-biphenylene

\[\text{4,4'}-\text{p-terphenylene}\]

and the like; a polyphenylene group in which 2 or more benzene rings are aligned and connected each other in their respective para-position through azo, azoxy, azomethine, ester or trans-vinylene bond, as, for example
and the like; and 2,6-naphthylene group. The remaining less than 50 mol % may be such member as p-phenylene, m-phenylene, o-phenylene or trans-1,4-cyclohexylene group. Since the component (A) is advantageously incorporated into the polyester resin as a polybasic acid component or a polyhydric alcohol component, said component (A) may preferably be derived from the compounds whose end groups are either member of carboxyl group, carboxylic ester group, acid chloride, hydroxyl group and acetyl group.

Typical compounds are as follows:

For a mesogenic group:

- HOOC-\(\text{C}_6\text{H}_4\)-COOH,
- \(\text{CH}_3\text{OOCC}_6\text{H}_4\)-COOCH\(_3\),
- \(\text{ClCO-}\text{C}_6\text{H}_4\)-COCl,
- \(\text{CH}_3\text{OOCC}_6\text{H}_4\)-COOCH\(_3\),
- \(\text{CH}_2\text{OOCC}_6\text{H}_4\)-COOCH\(_3\),
- \(\text{HOOC-}\text{C}_6\text{H}_4\)-COOH,
- \(\text{Cl-CO-}\text{C}_6\text{H}_4\)-COCl,
- \(\text{HO-}\text{C}_6\text{H}_4\)-OH,
- \(\text{CH}_3\text{O-C-}\text{C}_6\text{H}_4\)-COOCH\(_3\),
- \(\text{HO-}\text{C}_6\text{H}_4\)-OH,
- \(\text{HOOC-}\text{C}_6\text{H}_4\)-COOCH\(_3\).

These are only examples of the compounds which are used in this invention for the introduction of said A component and the invention can never be limited to the same.

The spacer component (B) may be represented by either formula:

\[ -(\text{CH}_2)_n- \quad \text{or} \quad -(\text{CH}_2\text{CH}_2\text{OH})_n\text{CH}_2\text{CH}_2- \]

This spacer component (B) should be connected to the aforesaid, (A) component and to the neighboring A-X-B unit through an ester bond. Therefore, the starting materials to be used for the introduction of said (B) should preferably be ended by OH, COOH or their reactive derivatives. Examples of such materials are as follows:

Compounds with \(-(\text{CH}_2)_n-\) group:
- ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-
nonanediol, 1,10-decanediol, 1,12-dodecanediol, adipic acid, sebacic acid, azelaic acid, and other aliphatic dicarboxylic acids and the like. Compounds with

\[ \text{diethylene glycol, triethylene glycol, tetraethylene glycol and the like.} \]

This type of polyester resins can be easily prepared in a conventional way, i.e. by the reaction of polybasic acids and polyhydric alcohols which are suitable for the introduction of said A and B components into the resins.

Usually, excess amounts of polyhydric alcohols are used with the polybasic acids and esterification or ester exchange reaction may be carried out at a temperature of 130° to 300° C., preferably under inert gas stream as nitrogen gas and in the presence of esterification catalyst or ester exchange catalyst. Examples of such catalysts are oxides or acetates of such metals as lead, zinc, manganese, barium, calcium, magnesium, lithium, germanium, antimony and the like, p-toluene sulfonic acid, alkyl titanates, organic tin compounds and the like. When used, the amount of such catalyst is preferably determined in a range of 0.01 to 0.5% by weight of the acid component used.

When an excess amount of polyhydric alcohol is used, a polyester resin having end hydroxyl groups results therefrom and such polyester resin may be further reacted with an acid anhydride to give a polyester with end carboxyl groups. As desired. It is, of course, possible to carry out the original esterification using an excess amount of acid component, and however, at that time, considerable difficulties are encountered in carrying out a uniform esterification because of limited solubility or sublimation tendency of the selected acid component. There always remains certain amounts of unreacted acid in the produced resin. Therefore, the said esterification is, in general, carried out by using an excess amount of polyhydric alcohol component as already stated herein before.

The thus obtained polyester resin is characterized in that the polymer chain is composed of a repeating unit comprising a comparatively rigid, planar structural mesogenic group (A) connected through an ester bond to a flexible spacer group (B), adjoining two repeating units are connected to each other through an ester bond, the end groups are OH, COOH or their reactive derivatives, and the sum of the resinous acid value and OH value is 10 to 200, preferably 20 to 100.

Therefore, the resin can exhibit enough thermosetting properties. As to the molecular weight, though it may be widely varied with the employed constituting elements, it is usually in a range of 500 to 20,000 in terms of number average molecular weight (polystyrene conversion). The phase transition point is usually in a range of about 80° to 230° C.

If desired, less than 50 mol % of said mesogenic group (A) may be substituted with p-phenylene, m-phenylene, o-phenylene or 1,4-cyclohexylene group, without the fear of losing the desired liquid crystalline properties. The second type of the present polyester resin comprises a repeating unit (I) of the formula: A-X-B in which A, B and X are as defined above, and a repeating unit (II) of the formula: R in which R is as defined hereinbefore, said unit (I) and unit (II) being contained in the weight ratio of (I)/(II) = 99.9/0.1 to 70/30, arranged in any random order and connected to each other through an ester bond, the end groups being OH, COOH or their reactive derivatives, the sum of resinous acid value and OH value being 10 to 200 and capable of forming an anisotropic molten phase.

In this type of resin, the meaning of mesogenic group A, spacer group B and the starting materials to be used for the introduction of said A and said B are the same as those of the first type polyester resin.

This resin is characterized in that besides the repeating unit of the formula: A-X-B (I), a second repeating unit (II) of the formula: R, i.e. bivalent to hexavalent aliphatic, aromatic or alicyclic residue which may contain up to 4 OH and/or COOH groups, is included in the weight ratio of said (I) to (II) of 99.9/0.1 to 70/30. Since a number of repeating units (I) of the formula: A-X-B and a repeating unit (II) of the formula: R are aligned in any successive order in the chain and connected each other through an ester bond, R must be bonded to the neighboring A, B or R through an ester bond, and therefore, the starting material used for the introduction of said R unit should preferably have at least two functional groups capable of participating in the formation of said ester bonding, as, for example, OH and COOH.

Examples of such materials are neopentyl glycol, di-methylol propionic acid, 1,4-cyclohexanediol, trimethylol ethane, trimethylol propane, glycerine, pentaerythritol, sorbitol and other similar alcohols; phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, tetrachlorophthalic anhydride, tetrafluorophthalic anhydride, p-hydroxy benzoic acid, hexahydrophthalic anhydride, 3-methylhexahydrophthalic acid, 4-methylhexahydrophthalic acid and other similar acids.

This type of polyester resin may be advantageously prepared by using appropriate alcohols and acids which are suitable for the introduction of said A, B and R components, and following the conventional way as in the first type of the present polyester resin.

The thus obtained polyester resin is characterized in that the polymer chain is composed of a repeating unit (I) comprising a comparatively rigid, planar structural mesogenic group (A) connected through an ester bond to a flexible spacer group (B) and a repeating unit (II) of the formula: R, which is a hydrocarbon residue used for the control of film properties, the weight ratio of said unit (I) to unit (II) being settled, from the standpoint of the liquid crystalline properties and film properties desired, in a range of 99.9/0.1 to 70/30, adjoining two repeating units are connected to each other through an ester bond, the end groups are OH, COOH or their reactive derivatives and the sum of resinous acid value and hydroxyl value in 10 to 200, preferably 30 to 150. Therefore, the resin can exhibit sufficient thermosetting properties. As to the molecular weight, it may be widely varied with the employed constituting elements and however, it is usually in a range of 500 to 10,000 in terms of number average molecular weight (polystyrene conversion). The phase transition point is usually in a range of about 80° to 230° C.

If desired, less than 50 mol % of said mesogenic group (A) may be substituted with p-phenylene, m-phenylene, o-phenylene or 1,4-cyclohexylene group, without the fear of losing the desired liquid crystalline properties.

In either type of the above-mentioned polyester resins, they are solid at room temperatures and excellent in
storage stability. Since a number of hydroxyl or carboxyl groups are included, they are used, together with a polyisocyanate compound or aminoplast resin or glycidyl bearing compound, for the preparation of thermosetting type coating compositions.

Furthermore, since they are liquid crystalline materials, the thus obtained coating compositions are excellent in flowability at the baking stage and can result in coatings with excellent gloss and appearance.

To make the most of the abovementioned characteristic features, the invention provides a powder coating resinous composition containing the present polyester resin. The present powder coating resinous compositions are classified in the following two groups depending on the type of hardener co-used. That is, the first type of powder coating resinous composition comprises a polyester resin comprising a repeating unit (I) of the formula: A-X-B (I) or a combination of the repeating unit (I) and a repeating unit (II) of the formula: R . . . (I), wherein 100 to 50 mol % of A stands for a mesogenic group selected from a polyphenylene group in which 2 or more benzene rings are alined and connected each other in their respective para-positions, a polyphenylene group in which 2 or more benzene rings are alined and connected each other in their respective para-positions through an azoxy, azoxy, ester or trans-vinylene bond, or a 2,6-naphthylene group, the remaining 50 mol % of A stands for a member selected from the group consisting of p-phenylene, m-phenylene, o-phenylene and trans 1,4-cyclohexylene; B is a spacer group represented by the formula: \(-\text{CH}_2\text{CH}_2\)- or 

\[-\text{CH}_3\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\,-\]

in which n is an integer of 2 to 20 and m is an integer of 1 to 19; X is an ester bond, and R stands for a bivalent to hexavalent aliphatic, aromatic or alicyclic hydrocarbon residue which may include up to 4 OH and/or COOH group, the weight ratio of said units (I) to units (II) being 99.9:0.1 ~ 70:30, adjoining two repeating units placed in random order being connected through an ester bond, the end bondings of the connected repeating units being occupied by OH or its reactive derivatives, the resinous OH value being 20 ~ 200, and being capable of forming an anisotropic molten phase and (b) a blocked isocyanate compound or an amino-plast resin. The the hydroxyl value of the polyester resin is preferably controlled in a range of 30 ~ 100 so as to give the optimum thermostetting and film properties. The number average molecular weight of the polyester resin is selected to be in a range of 500 ~ 10,000 and preferably 500 ~ 4,000.

Since the polyester resin is solid at room temperatures and contains a number of crystalline, rigid mesogenic groups, when combined with a blocked polyisocyanate compound or an aminoplast resin, the thus obtained resinous composition may be stably stored without any undesired blocking thereof. The reactivity of the polyester resin with the selected hardener is excellent because of the higher hydroxyl value. Since the resin can be converted to a low viscous liquid phase at once when applied heating (i.e. liquid crystalline properties), the composition can result in an amorphous, clear coating with an excellent appearance.

Furthermore, since the polyester resin includes a flexible spacer group and a hydrocarbon residue R which is useful as a film modifier, the thus formed coating is excellent in bending processability and other film properties. Thus, the composition is very useful as a resinous composition for a coating powder.

The compounding ratio of said polyester resin and polyisocyanate compound or aminoplast resin, compounding means and preparation of powder coating are not of specific and any conventional techniques may be satisfactorily used. The second type of the present powder coating resinous composition comprises (a) a polyester resin comprising a repeating unit (I) of the formula: A-X-B . . . (I) or a combination of the repeating unit (I) and a repeating unit (II) of the formula: R . . . (II), wherein 100 to 50 mol % of A stands for a mesogenic group selected from a polyphenylene group in which 2 or more benzene rings are alined and connected to each other in their respective para-positions, a polyphenylene group in which 2 or more benzene rings are alined and connected with each other in their respective para-position through an azoxy, azoxy, ester or trans-vinylene bond, or 2,6-naphthylene group, the remaining 50 mol % of A stands for a member selected from the group consisting of p-phenylene, m-phenylene, o-phenylene and trans 1,4-cyclohexylene; B is a spacer group represented by the formula: 

\[-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{CH}_2-\,-\]

in which n is an integer of 2 to 20 and m is an integer of 1 to 19; X is an ester bond, and R stands for a bivalent to hexavalent aliphatic, aromatic or alicyclic hydrocarbon residue which may include up to 4 OH and/or COOH group, the weight ratio of said units (I) to units (II) being 99.9:0.1 ~ 70:30, adjoining two repeating units placed in random order being connected through an ester bond, end bondings of the connected repeating units being occupied by OH, COOH or methylester group, resinous acid value being 15 ~ 100, and being capable of forming an anisotropic molten phase and (b) a compound or resin having at least 2 epoxy groups in the molecule thereof.

The resinous acid value of said polyester resin should be controlled in a range of 15 ~ 100, more preferably 30 ~ 70. This is because, if the resinous acid value is less than 15, there is a tendency that the mechanical strength of the coating be lowered, and if the resinous acid value exceeds the upper limit of 100, the storage stability of the composition is lowered, resulting in undesired blocking of the composition and uneven coating therefrom.

As to the molecular weight of the polyester resin, it may be widely varied with the employed constituting elements and however, the number average molecular weight (polystyrene conversion) is, most preferably, in a range of 500 ~ 4,000. The phase transition point should preferably be in a range of about 60 ~ 180° C.

Examples of the compound or resin having at least 2 epoxy groups are diglycidyl ethers of bisphenol A, diglycidyl ethers of bisphenol F, glycidyl esters and glycidyl polyglycidyl ethers of polyhydric alcohols as diglycidyl ethers of ethyleneglycol and triglycidyl ethers of trimethylol propane, diglycidyl esters of dibasic acids, such as the diglycidyl ester of terephthalic acid, the triglycidyl isocyanurate and the like. The compounding ratio of said polyester resin and epoxy compound or resin may be appropriately selected in a conventional way, in due consideration of the amounts of functional groups carried with these components.
Since the polyester resin is solid at room temperatures and contains a number of crystalline, rigid mesogenic groups, when combined with a polyepoxy compound or resin, the thus obtained resinos composition may be stably stored without any undesired blocking thereof.

The reactivity of the polyester resin with the selected hardener is excellent because of its higher acid value. Since the resin can be converted to a low viscous liquid phase at once when applied heating (i.e. liquid crystalline properties), the composition can result in an amorphous, clear coating with an excellent appearance.

Furthermore, since the polyester resin includes a flexible spacer group and a hydrocarbon residue which is useful as a film modifier, the thus formed coating is excellent in bending processability and other film properties. Thus, the composition is very useful as a resinos composition for a coating powder.

The invention shall be now more fully explained in the following Examples. Unless otherwise being stated, all parts and percentages are by weight.

**EXAMPLE 1**

Into a reaction vessel fitted with a heating device, a stirrer, a nitrogen gas inlet tube and a fractionating column, were placed 10 mols of dimethylester of 4,4'-diphenyl carboxylic acid, 11 mols of 1,9-nonanediol and 2.2 g of dibutyl tin oxide and the mixture was heated under nitrogen gas stream to obtain a melt. Then, an ester exchange reaction was carried out at 130° to 230° C. while removing the formed methanol out of the system.

After collecting 760 ml of methanol, the mixture was reacted at 230° C. under 10 mmHg for additional 1 hour to complete the ester exchange reaction.

Thus obtained polyester resin (1) had a hydroxyl value of 25 and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135° C. and trichlorobenzene solvent) of 6,800.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 148° C. and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at about 116° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

Thus obtained thermosetting polyester resin (1) capable of forming an anisotropic molten phase and CRELAN U1 (e-caprolactam blocked IPDI, NXO equivalent 36.5, trademark of Bayer) were compounded in a OH/NCO equivalent ratio of 1/1 and dibutyl tin dilaurate was added thereto as a curing catalyst in an amount corresponding to 1.0 wt% of the total solid.

The mixture was then heat-melted at 150° C., allowed to cool to solidify the same and then pulverized to powder having a mean diameter of 10μ or less. The powder was coated onto a tin plate and baked at 230° C. for 20 minutes. Thus obtained coating was clear and had a smooth surface. The polyester resin was thus proven to be useful as a thermosetting resin in powder coating.

Test results are shown in Table 1.

**EXAMPLE 2**

100 parts of the polyester (1) obtained in Example 1 were placed in a reaction vessel and while heating the polyester at 150° C. under dried nitrogen gas and maintaining it at a molten state, 6.65 parts of phthalic anhydride were added thereto and the mixture was reacted at the same temperature for 1 hour to obtain a polyester resin (2). Thus obtained polyester had a hydroxyl value of 1.0, an acid value of 22.0, and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135° C. and trichlorobenzene solvent) of 7,100.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at 148° C. and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at 108° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

Thus obtained thermosetting polyester resin (2) capable of forming an anisotropic molten phase and EPO-TOHTO YD-011 (epoxy resin, epoxy equivalent 475, trademark of Tohto Kasei) were compounded in a OH/-epoxy equivalent ratio of 1/1.

The mixture was then heat-melted at 130° C., allowed to cool to solidify the same and pulverized to powder having a mean diameter of 10μ or less.

The powder was coated onto a tin plate and baked at 230° C. for 20 minutes.

Thus obtained coating was evaluated as in Example 1 and the results shown were in Table 1.

**EXAMPLE 3**

Into a reaction vessel, were placed 3 mols of dimethyl ester of 4,4'-diphenyl carboxylic acid, 4 mols of 1,9-nonanediol and 0.8 g of dibutyl tin oxide and the mixture was heated under nitrogen gas stream to obtain a melt. Then, an ester exchange reaction was carried out at 130° to 230° C. while removing the formed methanol out of the system.

After collecting 230 ml of methanol, the mixture was reacted at 230° C. under 10 mmHg for additional 1 hour to complete the ester exchange reaction.

Thus obtained polyester had a hydroxyl value of 82, and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135° C. and trichlorobenzene solvent) of 1,550.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 138° C. and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at about 95° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

Thus obtained thermosetting polyester resin (3) was evaluated as in Example 1 and the test results were shown in Table 1.

**EXAMPLE 4**

100 parts of the polyester (3) obtained in Example 3 were placed in a reaction vessel and while heating the polyester at 130° C. under dried nitrogen gas and maintaining it at a molten state, 21.7 parts of phthalic anhydride were added thereto and the mixture was reacted at the same temperature for 1 hour to obtain a polyester resin (4). Thus obtained polyester had a hydroxyl value of 1.5, an acid value of 68.5, and a number average molecular weight (polystyrene conversion, measured
Thus obtained thermosetting polyester resin (4) was evaluated as in Example 2 and the results were shown in Table 1.

EXAMPLE 5

Into a reaction vessel, were placed 7 mols of dimethyl ester of 4,4'-diphenyl carboxylic acid, 8 mols of 1,8-octanediol and 1.5 g of dibutyl tin oxide and the mixture was heated under nitrogen gas stream to obtain a melt. Then, an ester exchange reaction was carried out at 130° to 230° C. while removing the formed methanol out of the system.

After collecting 530 ml of methanol, the mixture was reacted at 230° C. under 10 mmHg for an additional 1 hour to complete the ester exchange reaction.

Thus obtained polyester (5) had a hydroxyl value of 37, and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135° C. and trichlorobenzene solvent) of 4,000.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 180° C. and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at about 173° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

Thus obtained thermosetting polyester resin (5) was evaluated as in Example 1 and the results were shown in Table 1.

EXAMPLE 6

Into a reaction vessel, were placed 7 mols of dimethyl ester of 4,4'-diphenyl carboxylic acid, 8 mols of 1,6-hexanediol and 1.5 g of dibutyl tin oxide and the mixture was heated under nitrogen gas stream to obtain a melt. Then, an ester exchange reaction was carried out at 130° to 230° C. while removing the formed methanol out of the system.

After collecting 530 ml of methanol, the mixture was reacted at 230° C. under 10 mmHg for additional 1 hour to complete the ester exchange reaction.

Thus obtained polyester (6) had a hydroxyl value of 40, and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135° C. and trichlorobenzene solvent) of 4,250.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 215° C. and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at about 180° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.
Thus obtained polyester had a hydroxyl value of 30 and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135°C. and trichlorobenzene solvent) of 4,900.

When the polyester was heated at a rate of 10°C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 105°C. and when cooled at a rate of 10°C. per minute, a sharp and large exothermic peak at about 68°C. The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

Thus obtained thermosetting polyester resin was then evaluated as in Example 1 and the test results were shown in Table 1.

**EXAMPLE 10**

Into a reaction vessel, were placed a mixed solvent of 1,000 g toluene and 100 g pyridine, and then 0.5 mol of 4-4'-carbonyl chloride) benzoxyloxy) benzoic acid chloride and 0.55 mol of 1,9-nonanediol and the mixture was heated under dried nitrogen gas and reacted at 100°C. until the absorption peak at 1780cm^-1 (carboxylic chloride) in IR spectrum had disappeared to obtain a polyester resin (10). Thus obtained polyester had a hydroxyl value of 27, and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135°C. and trichlorobenzene solvent) of 5,300.

When the polyester was heated at a rate of 10°C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at 165°C. and when cooled at a rate of 10°C. per minute, a sharp and large exothermic peak at 134°C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

Thus obtained thermosetting polyester resin was then evaluated as in Example 1 and the results were shown in Table 1.

**COMPARATIVE EXAMPLE 1**

Into a reaction vessel, were placed 20 mols of dimethyl ester of 4,4'-diphenyl carboxylic acid, 21 mols of 1,6-hexanediol and 5.0 g of dibutyl tin oxide, and the mixture was heated under dried nitrogen gas to get a melt. Ester exchange reaction was carried out at 130°C. to 230°C. while removing the formed methanol out of the system.

After collecting 1,500 ml of methanol, the mixture was further heated at 230°C. and under 1 mmHg pressure for 5 hour to complete the ester exchange reaction.

Thus obtained polyester had a hydroxyl value of 8 and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135°C. and trichlorobenzene solvent) of 3,940.

When the polyester was heated at a rate of 10°C. per minute by using a differential scanning calorimetry, there was no definite endothermic peak and when cooled at a rate of 10°C. per minute, no definite exothermic peak.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols but no specific texture due to optical anisotropic property was observed. This resin was of amorphous nature and no phase transition point was observed.
EXAMPLE 11

Into a reaction vessel, were placed 7 mols of dimethyl ester of 1,10-decanedicarboxylic acid, 8 mols of 4,4'-biphenol and 1.5 g of dibutyl tin oxide, and the mixture was heated under dried nitrogen gas to get a melt. Ester exchange reaction was carried out at 150° to 250° C. while removing the formed methanol out of the system.

After collecting 500 ml of methanol, the mixture was further heated at 250° C. and under 10 mmHg pressure for 2 hours to complete the ester exchange reaction.

The reaction mixture was allowed to cool and 1,000 g of N-methylpyrrolidone were dropwise added at 200° C. and below.

To this mixture, 295 g of phthalic anhydride were added while keeping the temperature at 150° C. and the combined mixture was reacted at 150° C. for 1 hour and then dropwise added to a separate tank containing 5,000 ml of toluene. The precipitated resin was separated by filtration.

Thus obtained polyester resin (11) had a hydroxyl value of 0.1, an acid value of 35 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135° C. and tri chlorobenzene solvent) of 4,680.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimeter, there was a sharp and large exothermic peak at about 205° C. and when cooled at a rate of 10° C. per minute, a broad exothermic peak at about 183° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicos and specific texture due to optical anisotropic property was clearly observed.

Thus obtained thermosetting polyester resin was then evaluated as in Example 2 and the test results were shown in Table 1.

<table>
<thead>
<tr>
<th>Example 2</th>
<th>3</th>
<th>4</th>
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<th>6</th>
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<td>clear</td>
<td>clear</td>
<td>clear</td>
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<td>○</td>
<td>○</td>
<td>○</td>
<td>Δ</td>
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TABLE 1

<table>
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<th>11</th>
<th>12</th>
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<td>clear</td>
<td>slightly turbid</td>
<td>turbid</td>
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<td>flatness of film*</td>
<td>Δ</td>
<td>○</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

EXAMPLE 12

Into a reaction vessel, were placed 7 mols of dimethyl ester of 4,4'-diphenyl carboxylic acid, 7 mols of 1,8-octanediol, 1 mol of diethyleneglycol and 1.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt. Ester exchange reaction was carried out at 130° – 230° C. while removing the formed methanol out of the system.

After collecting 530 ml of methanol, the content was further reacted at 230° C. under 10 mmHg pressure for 1 hour to complete the ester exchange reaction.

Thus obtained polyester (12) had a hydroxyl value of 37 and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135° C. and trichlorobenzene solvent) of 4,900.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimeter, there was a sharp and large endothermic peak at 125° C., and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at 48° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicos and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 13

Into a reaction vessel, were placed 7 mols of dimethyl ester of 4,4'-diphenyl carboxylic acid, 6 mols of 1,6-hexanediol, 2 mols of triethylene glycol and 1.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt. Ester exchange reaction was carried out at 130° – 230° C. while removing the formed methanol out of the system.

After collecting 530 ml of methanol, the content was further reacted at 230° C. under 10 mmHg pressure for 1 hour to complete the ester exchange reaction.

Thus obtained polyester (13) had a hydroxyl value of 40 and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135° C. and trichlorobenzene solvent) of 4,250.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimeter, there was a main endothermic peak at about 155° C., and when cooled at a rate of 10° C. per minute, a main exothermic peak at 80° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicos and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 14

Into a reaction vessel, were placed 1,000 g of toluene and 100 g of pyridine, and then 0.5 mol of 4,4'-biphenyl carboxylic acid chloride and 0.55 mol of diethyleneglycol and the mixture was heated under dried nitrogen gas to 100° C. and reacted at the same temperature until the absorption peak in 1R at 1780 cm (corresponding to said carboxylic acid chloride) disappeared. Thereafter, the reaction mixture was dropwise added to 2,000 ml of methanol and the precipitates were filtered and dried to obtain a polyester resin (14).

Thus obtained polyester had a hydroxyl value of 30 and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135° C. and trichlorobenzene solvent) of 4,900.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimeter, there was a sharp and large endothermic peak at 125° C., and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at 48° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicos and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 15

Into a reaction vessel, were placed 7 mols of dimethyl ester of 1,10-decanedicarboxylic acid, 1 mol of 4-hydroxy benzoic acid, 7.5 mols of 4,4'-biphenol, 0.5 mol of trimethylol propane and 1.5 g of dibutyl tin oxide and
the mixture was heated under dried nitrogen gas to get a melt. Ester exchange reaction was carried out at 130° - 250° C. while removing the formed methanol out of the system.

After collecting 500 ml of methanol, the content was further reacted at 250° C. and under 10 mmHg pressure for 1 hour to complete the ester exchange reaction. The mixture was allowed to cool, while adding at 200° C. and below, 1,000 g of N-methyl pyrrolidone. This was then dropwise added to a separate tank containing 5,000 ml of methanol under stirring and the precipitated polymer was filtered and dried.

Thus obtained polyester (15) had a hydroxyl value of 52 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 4,680.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 155° C. and when cooled at a rate of 10° C. per minute, a sharp exothermic peak at about 123° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

**EXAMPLE 16**

Into a reaction vessel, were placed 5 mols of 2,6-naphthalene dicarboxylic acid, 6 mols of 1,9-nonanediol and 2.0 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt.

Ester exchange reaction was carried out at 130° - 230° C. while removing the formed methanol out of the system.

After collecting 350 ml of methanol, the content was further reacted at 230° C. and under 10 mmHg pressure for 1 hour to complete the ester exchange reaction.

Thus obtained polyester (16) had a hydroxyl value of 30 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 3,680.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 125° C. and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at about 49° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

**EXAMPLE 17**

Into a reaction vessel, were placed 640 parts of dimethyl ester of 4,4'-diphenyl carboxylic acid, 397 parts of 1,9-nonanediol, 29 parts of trimethyl propane and 0.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt.

Ester exchange reaction was carried out at 130° - 230° C. while removing the formed methanol out of the system.

After collecting 175 ml of methanol, the content was further reacted at 230° C. and under 10 mmHg pressure for 1 hour to complete the ester exchange reaction.

Thus obtained polyester (17) had a hydroxyl value of 50 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 4,500.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 138° C. and when cooled at a rate of 10° C. per minute, a sharp and large exothermic peak at about 110° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

Thus obtained, thermosetting polyester resin and CRELAN U1 (e-caprolactam blocked IPDI, NCO equivalent 365, trademark of Bayer) were combined together in a OH/NCO equivalent ratio of 1/1 and the mixture was added with dibutyl tin dilaurate in an amount corresponding to 1.0 wt % of the total weight of the combined mixture. This was then heat-melted at about 130° C., allowed to cool and pulverized to powder having an average diameter of 10μ or less. Thus obtained powder was applied onto a tin plate and baked at 180° C. for 20 minutes to obtain a coating, which was clear and smoothness.

The results were shown in Table 2.

**EXAMPLE 18**

100 parts of the polyester (17) obtained in Example 17 were placed in a reaction vessel and heated under dried nitrogen gas to 170° C. to get a melt.

To this, were added 18.7 parts of trimellitic anhydride and the mixture was reacted at 170° C. for 30 minutes to obtain a polyester (18).

Thus obtained polyester had a hydroxyl value of 1.0, an acid value of 85, and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 5,800.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a large endothermic peak at about 130° C., and when cooled at a rate of 10° C. per minute, a large exothermic peak at about 88° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was observed (not so clear).

Thus obtained polyester resin was then combined with EPOITOHTO YD-011 (epoxy resin, epoxy equivalent 475, trademark of Tohko Kasei) in a COOH/epoxy equivalent ratio of 1/1 and after melting at about 120° C., cooling and then pulverizing, powder with an average diameter of 10μ or less was obtained. This powder was then applied onto a tin plate and baked at 230° C. for 20 minutes. Thus formed coating was evaluated as in Example 17 and the test results were shown in Table 2.

**EXAMPLE 19**

100 parts of the polyester (17) obtained in Example 17 were placed in a reaction vessel and heated under dried nitrogen gas to 150° C.

To this, were added 14.4 parts of phthalic anhydride and the mixture was reacted at 150° C. for 30 minutes to obtain a polyester (19).

Thus obtained polyester had a hydroxyl value of 1.0, an acid value of 45, and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 4,740.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry,
there was a sharp and large endothermic peak at about 135°C, and when cooled at a rate of 10° C. per minute, a large exothermic peak at about 113° C. The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was observed (not so clear).

Thus obtained polyester resin was then combined with EPO-TOHTO YD-011 (epoxy resin, epoxy equivalent 475, trademark of Tohto Kasei) in a COOH/epoxy equivalent ratio of 1/1 and after melting at about 120°C, cooling and then pulverizing, powder with an average diameter of 10μm or less was obtained. This powder was then applied onto a tin plate and baked at 180°C for 20 minutes.

Thus formed coating was evaluated as in Example 17 and the test results were shown in Table 2.

**EXAMPLE 20~26**

Using the materials shown in Table 3, the same procedures as stated in Example 17 were repeated to obtain polyester resins (20~26).

Hydroxyl values, acid values, number average molecular weights, thermal properties tested by differential scanning calorimetry and microscopic observation results for these resins are shown in Table 4.

Thermosetting properties of these polyester resins were tested as in Example 17 and the results were shown in Table 2.

**EXAMPLE 27**

Into a reaction vessel, were placed 554 parts of dimethyl ester of sebacic acid, 487 parts of 4,4'-biphenol, 17.9 parts of trimethyl propane and 0.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt.

Ester exchange reaction was carried out at 130°~250°C while removing the formed methanol out of the system.

After collecting 186 ml of methanol, the content was further reacted at 250°C under 10 mmHg pressure for 2 hours to complete the ester exchange reaction.

The mixture was allowed to cool, while adding at 200°C and below, 1,000 parts of N-methyl pyrrolidone. 118 parts of phthalic anhydride were added at 150°C and reacted. This was then dropwise added to a separate tank containing 5,000 ml of toluene under stirring and the precipitated polymer was filtered and dried.

Thus obtained polyester (27) had a hydroxyl value of 1.0, an acid value of 45 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135°C and trichlorobenzene solvent) of 3,920.

When the polyester was heated at a rate of 10°C per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 205°C, and when cooled at a rate of 10°C per minute, a sharp exothermic peak at about 177°C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

The thermosetting properties of thus obtained resin were evaluated as in Example 18 and the test results were shown in Table 2.
### Table 3

<table>
<thead>
<tr>
<th>Example</th>
<th>Comp. Exam.</th>
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<tr>
<td>A</td>
<td>DPCDM (*1) dimethyl terephthalate dimethyl isophthalate NDCCl (*2) CHCDM (*3) SBADM (*4)</td>
</tr>
<tr>
<td>B</td>
<td>1,9-nonanediol 1,6-hexanediol triethyleneglycol tetraethyleneglycol 4,4'-biphenol</td>
</tr>
</tbody>
</table>

*1... dimethylster of 4,4'-diphenylcarboxylic acid
*2... 2,6-naphthalene dicarboxylic acid chloride
*3... dimethylster of trans-1,4-cyclohexane dicarboxylic acid
*4... dimethylster of sebacic acid

### Table 4

<table>
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<tr>
<th>Example</th>
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</table>

EXAMPLE 28

Into a reaction vessel, were placed 8 mols of 2,6-naphthalene dicarboxylic acid, 8.44 mols of 1,9-nonanediol, 0.46 mol of trimethyl propane and 1.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to obtain a melt. Thereafter, the mixture was reacted at 130°-230° C., while removing the formed water out of the system. After collecting 280 ml of water, the mixture was further reacted at 230° C. under 10 mmHg pressure for 1 hour to complete the esterification reaction and obtain a polyester resin (28).

Thus obtained polyester had a hydroxyl value of 42.65 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 5,680.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 124° C., and when cooled at a rate of 10° C. per minute, a sharp exothermic peak at about 43° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and a specific texture due to optical anisotropic property was clearly observed.

### Example 29

Into a reaction vessel, were placed 7 mols of dimethyl ester of 4,4'-diphenyl carboxylic acid, 8.44 mols of 1,9-nonanediol, 0.46 mol of trimethyl propane, 1 mol of dimethylester of trans-1,4-cyclohexane dicarboxylic acid and 1.5 g of dibutyl tin oxide and the mixture was...
heated under dried nitrogen gas to get a melt. Thereafter, the mixture was reacted at 130° to 230°C, while removing the formed methanol out of the system.

After collecting 610 ml of the formed methanol, the mixture was further reacted at 230°C under 10 mmHg pressure for 1 hour to complete the ester exchange reaction and obtain a polyester resin (9).

Thus obtained polyester had a hydroxyl value of 45 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135°C and trichlorobenzene solvent) of 4,500.

When the polyester was heated at a rate of 10°C per minute by using a differential scanning calorimetry, there was an endothermic peak at about 113°C, and when cooled at a rate of 10°C per minute, an exothermic peak at about 68°C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 30

Into a reaction vessel, were placed 1.0 mol of di-methyl ester of 4,4'-diphenyl carboxylic acid, 1.0 mol of 1,9-nonanediol, 0.1 mol of trimethylol propane and 0.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt. Temperature was gradually raised to 230°C, while removing methanol which was formed by an ester exchange reaction out of the system and the mixture was reacted at 230°C for 2 to 3 hours. 75 ml of methanol were collected.

Thereafter, the mixture was further reacted at 230°C, and under 10 mmHg pressure for 1 hour to complete the ester exchange reaction and obtain a polyester resin (P).

Next, 0.2 mol of trimellitic anhydride was added to the reaction mixture maintained at 180°C and the combined mixture was reacted at the same temperature for 90 minutes to obtain a polyester resin (30).

Thus obtained polyester had a hydroxyl value of 14, and acid value of 54 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135°C and trichlorobenzene solvent) of 5,200.

When the polyester was heated at a rate of 10°C per minute by using a differential scanning calorimetry, there was a large endothermic peak at about 130°C, and when cooled at a rate of 10°C per minute, a large exothermic peak at about 88°C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 31

To the polyester (P) obtained in Example 30 and maintained under dried nitrogen gas at 150°C and in molten state, 0.3 mol of phthalic anhydride was added and the combined mixture was reacted at 150°C for 60 minutes to obtain a polyester resin (31).

Thus obtained polyester had an acid value of 40 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135°C and trichlorobenzene solvent) of 4,740.

When the polyester was heated at a rate of 10°C per minute by using a differential scanning calorimetry, there was a sharp and large endothermic peak at about 135°C, and when cooled at a rate of 10°C per minute, a sharp and large exothermic peak at about 113°C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 32

Into a reaction vessel, were placed 1.0 mol of 2,6-naphthalenic dicarboxylic acid, 1.0 mol of 1,9-nonanediol, 0.1 mol of trimethylol propane and 0.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt. Thereafter, the temperature was gradually raised to 220°C, while removing the formed water out of the system and the mixture was reacted at 220°C for 3 hours. After collecting 34 ml of water, the mixture was further reacted at 220°C under 10 mmHg pressure for 1 hour to complete the esterification reaction.

Then, at 180°C, 0.25 mol of trimellitic anhydride were added under dried nitrogen gas and the combined was reacted for 90 minutes to obtain a polyester resin (32).

Thus obtained polyester had a hydroxyl value of 6, an acid value of 68 and a number average molecular weight (polystyrene conversion, measured by GPC using column temperature 135°C and trichlorobenzene solvent) of 5,400.

When the polyester was heated at a rate of 10°C per minute by using a differential scanning calorimetry, there was a large endothermic peak at about 112°C, and when cooled at a rate of 10°C per minute, a large exothermic peak at about 68°C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was observed (slightly unclear).

EXAMPLE 33

Into a reaction vessel, were placed 1.0 mol of di-methyl ester of 4,4'-diphenyl carboxylic acid, 1.0 mol of 1,9-nonanediol, 0.2 mol of trimethylol propane and 0.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt.

While removing the formed methanol out of the system, the mixture was gradually heated to 230°C and reacted at the same temperature for 2 hours. Total 72 ml of methanol were collected. Then, the mixture was further reacted at 230°C and under 10 mmHg pressure for 1 hour to complete ester exchange reaction, allowed to cool to 180°C, added under dried nitrogen gas 0.4 mol of trimellitic anhydride and the combined mixture was reacted for 90 minutes to obtain a polyester resin (33).

When the polyester was heated at a rate of 10°C per minute by using a differential scanning calorimetry, there was a large endothermic peak at about 130°C, and when cooled at a rate of 10°C per minute, a large exothermic peak at about 58°C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 34

Into a reaction vessel, were placed 0.6 mol of dimethyl ester of 4,4'-diphenyl carboxylic acid, 0.4 mol of dimethylester of terephthalic acid, 1.0 mol of 1,9-nonanediol, 0.1 mol of trimethylol propane and 0.5 g of...
dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt. While removing the formed methanol out of the system, the mixture was gradually heated to 230° C. and reacted at the same temperature for 2 hours. Total 73 ml of methanol were collected. Then, the mixture was further reacted at 230° C. and under 10 mmHg pressure for 1 hour to complete ester exchange reaction, allowed to cool to 170° C., added under dried nitrogen gas 0.3 mol of phthalic anhydride and the combined mixture was reacted for 60 minutes to obtain a polyester resin (34).

Thus obtained polyester had an acid value of 44 and a number average molecular weight (polystere conver-10sion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 4,230.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was an endothermic peak at about 118° C. and when cooled at a rate of 10° C. per minute, an exothermic peak at about 65° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 35

Into a reaction vessel, were placed 0.8 mol of dit-15hyl ester of 4,4'-diphenyl carboxylic acid, 0.2 mol of dimethyl ester of trans-1,4-cyclohexene carboxylic acid, 1.0 mol of 1,6-hexadiol, 0.1 mol of trimethyl propane and 0.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt. While removing the formed methanol out of the system, the mixture was gradually heated to 240° C. and reacted at the same temperature for 4 hours. Total 70 ml of methanol were collected. Then, the mixture was further reacted at 240° C. and under 10 mmHg pressure for 1 hour to complete ester exchange reaction, allowed to cool to 150° C., added under dried nitrogen gas 0.25 mol of phthalic anhydride and the combined mixture was reacted for 60 minutes to obtain a polyester resin (35).

Thus obtained polyester had a hydroxyl value of 7, an acid value of 34 and a number average molecular weight (polystere conversion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 4,000.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was a large endothermic peak at about 145° C. and when cooled at a rate of 10° C. per minute, a large exothermic peak at about 53° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

EXAMPLE 36

Into a reaction vessel, were placed 1.0 mol of di-methyl ester of 4,4'-diphenyl carboxylic acid, 1.0 mol of 1,5-nonanediol, 0.1 mol of trimethylol propane and 0.5 g of dibutyl tin oxide and the mixture was heated under dried nitrogen gas to get a melt. While removing the formed methanol out of the system, the mixture was gradually heated to 230° C. and reacted at the same temperature for 2 hours. Total 72 ml of methanol were collected. Then, the mixture was further reacted at 230° C. and under 10 mmHg pressure for 1 hour to complete ester exchange reaction, allowed to cool to 180° C., added under dried nitrogen gas 0.3 mol of tetrachlorophthalic anhydride and the combined mixture was reacted for 2 hours to obtain a polyester resin (36).

Thus obtained polyester had an acid value of 37 and a number average molecular weight (polystere conversion, measured by GPC using column temperature 135° C. and trichlorobenzene solvent) of 5,690.

When the polyester was heated at a rate of 10° C. per minute by using a differential scanning calorimetry, there was an endothermic peak at about 133° C. and when cooled at a rate of 10° C. per minute, an exothermic peak at about 67° C.

The resin was then examined by using a microscope equipped with a heating stage under crossed nicols and specific texture due to optical anisotropic property was clearly observed.

SYNTHETIC EXAMPLES 1 – 4 (FOR COMPARISON)

Using the materials shown in Table 5 and adding 0.1 part of dibutyl tin oxide as a catalyst, esterification was carried out at 240° – 250° C.

After collecting theoretical amounts of formed water, the reaction mixture was further reacted under 16 – 20 mmHg pressure for about 5 hours. By this means, polyester resins F – I were prepared. The characteristics of these resins are shown in Table 6.

SYNTHETIC EXAMPLE 5 (FOR COMPARISON)

Using the materials shown in Table 5 and adding 0.1 part of dibutyl tin oxide as a catalyst, ester exchange reaction was carried out at 220° – 230° C.

After collecting theoretical amounts of formed methanol, the reaction mixture was further reacted at 240° – 250° C. and under reduced pressure of 16 – 20 mmHg for about 5 hours to obtain a polyester resin (J).

The characteristics of the resin are shown in Table 6.

| TABLE 5 |
|---|---|---|---|---|---|
| | Comparative Example | 7 | 8 | 9 | 10 |
| terephthalic acid | 166 | 166 | 166 | 166 | 78 |
| dimethyl terephthalate | 33 | 33 | 33 | 33 | 33 |
| isophthalic acid | 78 | 78 | 78 | 78 | 78 |
| dimethyl isophthalate | 29 | 29 | 29 | 29 | 29 |
| adipic acid | 71 | 71 | 71 | 71 | 71 |
| 1,6-hexanediol | 106 | 95 | 136 | 136 | 136 |
| 1,4-butanediol | 45 | 63 | 27 | 27 | 27 |
| ethylene glycol | 10 | 10 | 10 | 10 | 10 |
| neopentyl glycol | 40 | 40 | 40 | 40 | 40 |
| trimethyl propane | | | | | |

Numerical figure is given by weight.

| TABLE 6 |
|---|---|---|---|---|---|
| Polyester resin | F | G | H | I | J |
| OH value | 13 | 36 | 26 | 50 | 28 |
| number average molecular weight (GPC) | 7200 | 2800 | 3800 | 2300 | 3700 |
| DSC – endothermic peak temperature (°C) | no | no | no | no | no |
| exothermic peak temperature (°C) | peak | peak | peak | peak | peak |
| anisotropic property | no | no | no | no | no |
SYNTHETIC EXAMPLE 6 (FOR COMPARISON)

Into a reaction vessel, were placed 83 parts of ethyleneglycol, 327 parts of neopentyl glycol, 435 parts of dimethyl terephthalate and 0.4 part of zinc acetate and the mixture was heated under dried nitrogen gas to get a melt.

While removing the formed methanol out of the system, the temperature was gradually raised to 210°C and the mixture was reacted at the same temperature for 2 hours. Then, 6 parts of trimethyl propane, 149 parts of terephthalic acid, 224 parts of isophthalic acid and 0.5 part of dibutyl tin oxide were added and the combined mixture was heated to 240°C in 8 hours, reacted at the same temperature until the resinous acid value reached 7, allowed to cool to 180°C, added under dried nitrogen gas with 29 parts of trimellitic anhydride and further reacted for 90 minutes to obtain a polyester resin (K).

Thus obtained polyester had a hydroxyl value of 5, an acid value of 23, and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135°C and trichlorobenzene solvent) of 6,590.

However, this polyester was an amorphous, clear resin and showed no endothermic peak in a differential scanning calorimetric analysis.

The resin was also examined by using a microscope equipped with a heating stage under crossed nicks, and however, the characteristic texture due to optical anisotropic property was not observed.

SYNTHETIC EXAMPLE 7 (FOR COMPARISON)

Into a reaction vessel, were placed 136 parts of ethyleneglycol, 253 parts of neopentyl glycol, 472 parts of dimethyl terephthalate, 29 parts of 1,6-hexanediol and 0.4 part of zinc acetate and the mixture was heated under dried nitrogen gas to get a melt.

While removing the formed methanol out of the system, the temperature was gradually raised to 210°C and the mixture was reacted at the same temperature for 2 hours. Then, 20 parts of trimethyl propane, 308 parts of terephthalic acid, 224 parts of isophthalic acid and 0.5 part of dibutyl tin oxide were added and the combined mixture was heated to 240°C in 8 hours, reacted at the same temperature until the resinous acid value reached 6, allowed to cool to 200°C, added under dried nitrogen gas with 120 parts of trimellitic anhydride and further reacted for 90 minutes to obtain a polyester resin (L).

Thus obtained polyester had an acid value of 50, and a number average molecular weight (polystyrene conversion, measured by GPC of column temperature 135°C and trichlorobenzene solvent) of 5,700.

However, this polyester was an amorphous, clear resin and showed no endothermic peak in a differential scanning calorimetric analysis.

The resin was also examined by using a microscope equipped with a heating stage under crossed nicks, and however, the characteristic texture due to optical anisotropic property was not observed.

EXAMPLE 37–49

In each of the examples, the materials shown in Table 7 were pre-mixed in the indicated amounts and the pre-mix was melt-kneaded by using PR-46 type co-kneader (Bus Corp.) at the indicated temperature. After cooling, the solidified mass was pulverized and sieved by using 150 mesh net to obtain a powder coating having an average diameter of 150 mesh or less.

Thus obtained powder was applied onto a soft steel plate by using an electrostatic powder coating equipment, and the coated plate was baked at 230°C for 5 minutes to obtain a coating.

Storage stability of such powder coating and film properties of thus obtained coating were evaluated and the test results were shown in Table 8.

COMPARATIVE EXAMPLE 7–11

The same procedures as stated in Examples 37–49 were repeated using the materials shown in Table 7 as well as resin F, G, H, I or J.

The storage stability of the respective coating powder and film properties are shown in Table 8.

\n
<table>
<thead>
<tr>
<th>TABLE 7</th>
</tr>
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<tbody>
<tr>
<td>Example</td>
</tr>
<tr>
<td>37 38 39 40 41</td>
</tr>
<tr>
<td>polyester resin amounts</td>
</tr>
<tr>
<td>89 71 84 83 88</td>
</tr>
<tr>
<td>hardener</td>
</tr>
<tr>
<td>CRELAN UI KL-2525 levelling agent Ac4F curing catalyst DBTL titanium oxide JR-600 kneading temperature (°C.)</td>
</tr>
<tr>
<td>11 1 0.3 50 150</td>
</tr>
<tr>
<td>11 1 0.3 50 140</td>
</tr>
<tr>
<td>11 1 0.3 50 140</td>
</tr>
<tr>
<td>11 1 0.3 50 140</td>
</tr>
<tr>
<td>11 1 0.3 50 140</td>
</tr>
</tbody>
</table>

<table>
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</tr>
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<td>42 43 44 45 46</td>
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<td>88 87 88 75 87</td>
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<td>hardener</td>
</tr>
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</tr>
<tr>
<td>12 1 0.3 50 110</td>
</tr>
<tr>
<td>12 1 0.3 50 130</td>
</tr>
<tr>
<td>12 1 0.3 50 160</td>
</tr>
<tr>
<td>12 1 0.3 50 160</td>
</tr>
<tr>
<td>12 1 0.3 50 160</td>
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<td>47 48 49</td>
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<tr>
<td>polyester resin amounts</td>
</tr>
<tr>
<td>79 77 77</td>
</tr>
<tr>
<td>hardener</td>
</tr>
<tr>
<td>CRELAN UI KL-2525 levelling agent Ac4F curing catalyst DBTL titanium oxide JR-600 kneading temperature (°C.)</td>
</tr>
<tr>
<td>21 1 0.3 50 130</td>
</tr>
<tr>
<td>21 1 0.3 50 140</td>
</tr>
<tr>
<td>21 1 0.3 50 120</td>
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<table>
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<th>Comparative Example</th>
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<td>7 8 9 10 11</td>
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<tr>
<td>polyester resin amounts</td>
</tr>
<tr>
<td>F G H I J</td>
</tr>
<tr>
<td>92 85 84 74 88</td>
</tr>
<tr>
<td>hardener</td>
</tr>
<tr>
<td>CRELAN UI KL-2525 levelling agent Ac4F curing catalyst DBTL titanium oxide</td>
</tr>
<tr>
<td>8 1 0.3 50</td>
</tr>
<tr>
<td>15 1 0.3 50</td>
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<td>16 1 0.3 50</td>
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<td>26 1 0.3 50</td>
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<tr>
<td>26 1 0.3 50</td>
</tr>
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</table>
TABLE 7-continued

JR-600 kneading temperature (°C.)

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<th>Temperature (°C.)</th>
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<th>110</th>
<th>150</th>
<th>110</th>
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TABLE 8

Example

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<thead>
<tr>
<th>Flattness</th>
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<th>39</th>
<th>40</th>
<th>41</th>
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<tbody>
<tr>
<td>60° specular reflectance (%)</td>
<td>95</td>
<td>92</td>
<td>96</td>
<td>89</td>
<td>91</td>
</tr>
<tr>
<td>Erichsen (mm)</td>
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<td>&gt;9</td>
<td>&gt;9</td>
<td>&gt;9</td>
<td>&gt;9</td>
</tr>
<tr>
<td>Impact strength (kg · cm)</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
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<tr>
<td>Bending property</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Blocking resistance</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
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</table>

Table 8

Example

<table>
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<tr>
<th>Flattness</th>
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<th>43</th>
<th>44</th>
<th>45</th>
<th>46</th>
</tr>
</thead>
<tbody>
<tr>
<td>60° specular reflectance (%)</td>
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<td>93</td>
<td>92</td>
<td>92</td>
<td>93</td>
</tr>
<tr>
<td>Erichsen (mm)</td>
<td>&gt;9</td>
<td>&gt;9</td>
<td>&gt;9</td>
<td>&gt;9</td>
<td>&gt;9</td>
</tr>
<tr>
<td>Impact strength (kg · cm)</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
</tr>
<tr>
<td>Bending property</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Blocking resistance</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
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</table>

TABLE 9-continued

Example

<table>
<thead>
<tr>
<th>TGIC *4</th>
<th>10</th>
<th>12</th>
<th>16</th>
<th>5</th>
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<tbody>
<tr>
<td>Leveling agent Acronal *5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

Example

<table>
<thead>
<tr>
<th>Polyester resin (37)</th>
<th>(37)</th>
<th>(38)</th>
</tr>
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<tbody>
<tr>
<td>Amounts</td>
<td>35</td>
<td>90</td>
</tr>
<tr>
<td>Hardener EPICOAT 1002 *1</td>
<td>28</td>
<td></td>
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<tr>
<td>EPICOAT 1001 *2</td>
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<td></td>
</tr>
<tr>
<td>EPICOAT 828 *3</td>
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</tr>
<tr>
<td>TGIC *4</td>
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<td></td>
</tr>
<tr>
<td>Leveling agent Acronal *5</td>
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<td></td>
</tr>
<tr>
<td>Titanium dioxide</td>
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TABLE 10-continued

Example

<table>
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<th>51</th>
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<th>53</th>
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<tbody>
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<td>94</td>
<td>93</td>
<td>96</td>
</tr>
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<td>Erichsen (mm)</td>
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<td>&gt;9</td>
<td>&gt;9</td>
<td>&gt;9</td>
<td>&gt;9</td>
</tr>
<tr>
<td>Impact strength (kg · cm)</td>
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<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
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<tr>
<td>Bending property</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Blocking resistance</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

TABLE 9

Example

<table>
<thead>
<tr>
<th>Polyester resin amounts (32) (33) (34) (35) (36)</th>
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</thead>
<tbody>
<tr>
<td>30</td>
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</tbody>
</table>

Example

<table>
<thead>
<tr>
<th>Polyester resin amounts (33) (34) (35) (36)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
</tr>
</tbody>
</table>

Example

<table>
<thead>
<tr>
<th>Polyester resin amounts (34) (35) (36)</th>
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</thead>
<tbody>
<tr>
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</table>

Example

<table>
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<tr>
<th>Polyester resin amounts (35) (36)</th>
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<tbody>
<tr>
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Example

<table>
<thead>
<tr>
<th>Polyester resin amounts (36)</th>
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<tr>
<td>30</td>
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</tbody>
</table>

Example

<table>
<thead>
<tr>
<th>Polyester resin amounts (37)</th>
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<tr>
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</tbody>
</table>

Example

<table>
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<tr>
<th>Polyester resin amounts (38)</th>
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<tbody>
<tr>
<td>30</td>
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</table>

Examples 50-57 and Comparative Examples 12-14

Using the materials shown in Table 9 and following the procedures given in Examples 37-49, various powder coatings were prepared.

Each powder was then applied onto a zinc phosphate treated steel plate (0.8 mm thickness) by using an electrostatic powder coating equipment so as to give a dry film thickness of 50-60 μm and the coated plate was baked at 200° C. for 20 minutes.

These powder coatings and film properties were evaluated and the test results were shown in Table 10.

Since the present polyester resins have the characteristic liquid crystalline properties, when they are used as binder resins for powder coatings thus obtained powder coatings are excellent in storage stability and can give excellent coatings.

Therefore, such powders are very useful as precoat metal powder coatings.

What is claimed is:

I. A thermosetting polyester resin comprising a repeating units of the formula: A-X-B, wherein 100 to 50
mol % of A stands for a mesogenic group selected from a polyphenylene group in which 2 or more benzene rings are aligned and connected to each other in their respective para-positions, a polyphenylene group in which 2 or more benzene rings are aligned and connected to each other in their respective para-positions through an azo, azoxy, azomethine, ester or trans-vinylene bond, or a 2,6-naphthylene group, the remaining 50 mol % of A stands from a member selected from the group consisting of p-phenylene, m-phenylene, o-phenylene and trans 1,4-cyclohexylene; B is a spacer group represented by the formula: \(-(CH_2)_n\) or \(-(CH_2)_m\) with \(n\) an integer of 2 to 20 and \(m\) an integer of 1 to 19; and X is an ester bond, the adjoining two repeating units being connected through an ester bond, the end bondings of the connected repeating units being occupied by OH, COOH or their reactive derivatives, the sum of resinous acid value and OH value being 10 - 200, and being capable of forming an anisotropic molten phase, said thermosetting polyester resin having a transition point of 80° - 230°C, a number average molecular weight of 500 - 20,000, providing that when A is p-phenylene, n is an integer of 8 to 20.

2. A thermosetting polyester resin comprising a combination of repeating units of the formula: A-X-B...1\), wherein 100 to 50 mol % of A stands for a mesogenic group selected from a polyphenylene group in which 2 or more benzene rings are aligned and connected to each other in their respective para-positions, a polyphenylene group in which 2 or more benzene rings are aligned and connected to each other in their respective para-positions through an azo, azoxy, azomethine, ester or trans-vinylene bond, or a 2,6-naphthylene group, the remaining 50 mol % of A stands from a member selected from the group consisting of p-phenylene, m-phenylene, o-phenylene and trans 1,4-cyclohexylene; B is a spacer group represented by the formulas:

\[-(CH_2)_n\] or \[-(CH_2)_m(CH_2)O(CH_2)H_2\] ,

in which \(n\) is an integer of 2 to 20 and \(m\) is an integer of 1 to 19; and X is an ester bond, and a repeating unit of the formula: R...II, wherein R stands for a bivalent to hexavalent aliphatic, aromatic or alicyclic hydrocarbon residue which may include up to 4 OH and/or COOH groups, the weight ratio of said units (I) to (II) being 99.9:0.1 - 70:30, the adjoining two repeating units placed in random order being connected through an ester bond, the end bondings of the connected repeating units being occupied by OH, COOH or their reactive derivatives, the sum of the resinous acid value and OH value being 30 - 150, and being capable of forming an anisotropic molten phase, said thermosetting polyester resin having a transition point of 80° - 230°C, a number average molecular weight of 500 - 10,000, provided that when A is p-phenylene, n is an integer of 8 to 20.